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# Drastic reduction in the surface recombination velocity of crystalline silicon passivated with catalytic chemical vapor deposited $SiN_x$ films by introducing phosphorous catalytic-doped layer

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We improve the passivation property of n-type crystalline silicon (c-Si) surface passivated with a catalytic chemical vapor deposited (Cat-CVD) Si nitride ($SiN_x$) film by inserting a phosphorous (P)-doped layer formed by exposing c-Si surface to P radicals generated by the catalytic cracking of $PH_3$ molecules (Cat-doping). An extremely low surface recombination velocity (SRV) of 2 cm/s can be achieved for 2.5 Ω cm n-type (100) floating-zone Si wafers passivated with $SiN_x$/P Cat-doped layers, both prepared in Cat-CVD systems. Compared with the case of only $SiN_x$ passivated layers, SRV decreases from 5 cm/s to 2 cm/s. The decrease in SRV is the result of field effect created by activated P atoms (donors) in a shallow P Cat-doped layer. Annealing process plays an important role in improving the passivation quality of $SiN_x$ films. The outstanding results obtained imply that $SiN_x$/P Cat-doped layers can be used as promising passivation layers in high-efficiency n-type c-Si solar cells. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4891237]

## I. INTRODUCTION

n-type crystalline silicon (c-Si) has recently become more and more attractive to photovoltaic research, raising forecast of switch from p-type to n-type c-Si solar cells on photovoltaic industry.[1,2] Up to date, n-type c-Si solar cells are available, but their market share is at very low level (around 4%).[2] Nevertheless, the highest-efficiency solar cell has been recorded for an a-Si/n-type c-Si heterojunction back-contact solar cell in 2014.[3] n-type c-Si solar cells have many advantages for realizing higher conversion efficiency than p-type wafer cells, such as no light-induced degradation and less effect of metal impurities, and their market share will thus increase in the near future, along with decrease in their process cost.[1,4] Excellent passivation technique is of great importance particularly in improving back-contact c-Si solar cell efficiency. High-efficiency solar cells require surface passivation films not only with high transparency but also with high passivation ability so that photo-generated carriers do not recombine at the c-Si surface.[5] Catalytic chemical vapor deposition (Cat-CVD),[6] also referred to as hot-wire CVD, promises potential applications in passivation technique for c-Si solar cells. The world's best level of an surface recombination velocity (SRV) of 1.5 cm/s has been obtained for n-type c-Si wafers passivated with Cat-CVD $SiN_x$/amorphous-silicon (a-Si) stacked layers.[7] Cat-CVD can also be used to form a shallow phosphorous (P)-doped layer, called P Cat-doped layer, at a low substrate temperature, such as room temperature.[8,9] The shallow P doped layer can induce field-effect passivation, which can significantly suppress the recombination of minority carriers at c-Si surface. Although the shallow doping can be realized by other techniques, such as plasma doping, atomic layer deposition of dopants, and molecular beam epitaxy,[10–14] Cat-doping can significantly avoid damage onto c-Si surface induced by energetic ions since gas molecules are decomposed on a hot wire by catalytic reaction. The advantage makes Cat-doping become a favorable method for the formation of field-effect passivation layers for c-Si. Regarding the application of P Cat-doped layers to passivation technique, it has been already reported that the addition of P Cat-doped layers can reduce the SRV of n-type c-Si passivated with an a-Si film from 5 cm/s to 3 cm/s.[15] In our previous work, we have optimized $SiN_x$ passivation films with refractive index of ∼2.0 at wavelength of 630 nm prepared by Cat-CVD for n-type c-Si wafers.[16] The highest effective minority carrier lifetime ($\tau_{eff}$) of 3 ms, corresponding to a low SRV of 5 cm/s, can be obtained for n-type c-Si passivated with Cat-CVD $SiN_x$ films deposited at a low substrate temperature (∼100 °C) and post annealing. The use of $SiN_x$ films, whose refractive indexes are adjusted to be 2.0 even after decreasing the substrate temperatures, can avoid optical loss due to parasitic absorption in a-Si for $SiN_x$/a-Si stacked passivation system. The Cat-CVD $SiN_x$ films with high passivation quality and high transparency are suitable for application to c-Si solar cells. As we mentioned above, a P Cat-doped layer can induce field-effect passivation, which is effective in suppressing surface recombination by sending electrons away from the c-Si surface. In this study, in order to obtain even lower SRV on c-Si surface passivated with a $SiN_x$ film, we attempt to apply P Cat-doping for field-effect passivation. The results obtained show that the passivation quality of the $SiN_x$/P Cat-doped layer/c-Si structure significantly depends on the amount of activated donors in a P Cat-doped layer. Doped substrate temperature and annealing before depositing $SiN_x$ films are important parameters for

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TABLE I. Sample preparation conditions for P Cat-doping and the deposition of $SiN_x$ and a-Si films.

| | Doping | a-Si | $SiN_x$ |
|---|---|---|---|
| Gas sources | $PH_3$ 20 sccm | $SiH_4$: 10 sccm | $SiH_4$: 8 sccm $NH_3$: 150 sccm |
| Substrate temperature | 80–300 °C | 90 °C | 100 °C |
| Pressure | 1.0 Pa | 0.55 Pa | 10 Pa |
| Catalyzer temperature | 1300 °C | 1800 °C | 1800 °C |
| Time | 30–120 s | 30 s | 184 s |

activating P as donors. The deposition of $SiN_x$ films and post annealing at 350 °C for 30 min are necessary to achieve better interface properties and resulting high $\tau_{eff}$.[16] By the field-effect passivation and defect termination by H atoms, $\tau_{eff}$ of as high as 7 ms can be obtained, which corresponds to an SRV of ~2 cm/s.

## II. EXPERIMENTAL PROCEDURE

Sample preparation conditions are summarized in Table I. All c-Si wafers were first cleaned in diluted (5%) hydro-fluoric acid (HF) solution for 10 s to remove native oxide. P Cat-doped layers, $SiN_x$ films, and a-Si films were prepared in separate Cat-CVD chambers. A 2.25% helium diluted $PH_3$ was used as gas source for doping process. In this study, we changed the properties of P Cat-doped layers by changing substrate temperature ($T_{s\text{-}dope}$) and doping time ($t_{dope}$). The deposition condition of $SiN_x$ films and annealing conditions for the samples after depositing the $SiN_x$ films were same as the optimized conditions, under which high $\tau_{eff}$ of 3 ms can be obtained for a $SiN_x$/c-Si structure.[16] 290–$\mu$m-thick n-type (100) floating-zone (FZ) Si wafers with a resistivity of 2.5 Ω cm and a bulk minority carrier lifetime of >10 ms were used for the investigation of the passivation quality. The structure for $\tau_{eff}$ measurement is shown in Fig. 1. In order to investigate the effect of annealing on passivation quality, the P Cat-doped samples were annealed before and after depositing $SiN_x$ films. In this paper, we refer them to "annealing A" and "annealing B," respectively. Annealing A and annealing B were both conducted in a horizontal tubular furnace in nitrogen atmosphere. We prepared two samples under the same P doping condition at the same batch; one is for a sample with only annealing B, and the other is for a sample with both annealing A and B. The samples without annealing A were passivated with $SiN_x$ films immediately after P Cat-doping without air break, while the samples with annealing A were taken out from the P doping chamber, followed by furnace annealing and then $SiN_x$ deposition without any additional cleaning prior to deposition. All the $SiN_x$-deposited samples were finally annealed at 350 °C for 30 min (annealing B). The $\tau_{eff}$ was measured by microwave photo-conductivity decay ($\mu$-PCD) (KOBELCO LTA-1510EP) using a 904 nm wavelength pulse laser with a photon density of $5 \times 10^{13}\,cm^{-2}$, and then was evaluated from the exponential decay of the microwave reflection intensity. The $\tau_{eff}$ was measured in position-dependent mapping mode, and $\tau_{eff}$ shown below is the maximum value in the $20 \times 20\,mm^2$ area mapping. The relationship between $\tau_{eff}$ and SRV is described as

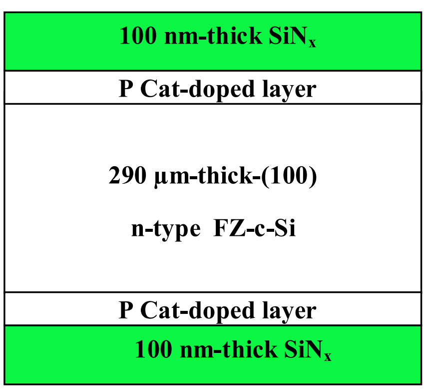


FIG. 1. The cross-sectional schematic of a sample for $\tau_{eff}$ measurement.

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2SRV}{W}, \tag{1}$$

where $\tau_{bulk}$ and $W$ represent minority carrier lifetime in bulk c-Si and wafer thickness, respectively. In this study, we calculated SRV by assuming $\tau_{bulk} = \infty$. We also measured excess-carrier-density-($\Delta n$-) dependent $\tau_{eff}$ by quasi-steady-state photoconductance (QSSPC) (WCT-120, Sinton Instruments).

We employed the Hall effect measurement to evaluate the sheet carrier density ($N_D$) of doped samples and secondary ion mass spectrometry (SIMS) for P concentration. The properties of c-Si wafers used for SIMS measurement are same as those used for $\tau_{eff}$ measurement. The SIMS measurement was performed from the back side of the samples after removing most of Si wafers in order to avoid the effect of knock-on and resulting unintentional broadening of P profiles. We used 2900 Ω cm p-type FZ c-Si wafers for the Hall effect measurement. The capture of carriers at defects on c-Si surface and oxidization may affect significantly the results of the Hall effect measurement.[8,17,18] In order to prevent these effects, a 10-nm-thick a-Si film was deposited on c-Si immediately after P doping without air exposure. In order to know the effect of annealing on $N_D$, samples were annealed at 350 °C before and after depositing a-Si films. Four Al electrodes were formed by evaporation through a metal hard mask to form the van der Pauw configuration. The samples were annealed at 350 °C for 1 min to make Ohmic contact between Al electrodes and a P Cat-doped layer. Figure 2 shows the cross-sectional schematic of a sample for the Hall effect measurement. The details of the measurement have been described in Ref. 8. The effect of H etching on the

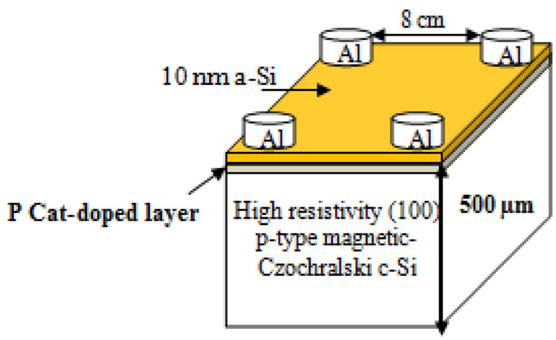


FIG. 2. The cross-sectional schematic of a sample for Hall measurement.

morphology of c-Si surface after P Cat-doping was evaluated by atomic force microscopy (AFM).

## III. RESULTS AND DISCUSSION

### A. The effect of annealing on P activation as donors and the passivation characteristic of $SiN_x$/P Cat-doped layer/c-Si structures

Annealing plays an important role in improving the passivation quality of $SiN_x$/c-Si structures.[16,19,20] In this study, we first investigate the effect of annealing. c-Si wafers received P Cat-doping at a $T_{s\text{-}dope}$ of 80 °C for 1 min, followed by $SiN_x$ film deposition. The samples were then annealed (annealing B) at various annealing temperatures ($T_{aB}$) for 30 min. Figure 3 shows the dependence of $\tau_{eff}$ of a $SiN_x$/P Cat-doped layer/c-Si structure on $T_{aB}$. The $\tau_{eff}$ of $SiN_x$/c-Si structures as a function of $T_{aB}$ is also shown for comparison. $\tau_{eff}$ starts to increase when $T_{aB}$ exceeds 200 °C for both structures. $\tau_{eff}$ reaches the highest value at a $T_{aB}$ of 350 °C, and then decreases with further increase in $T_{aB}$. The improvement in the $\tau_{eff}$ of the $SiN_x$/c-Si structure is supposed to be due to the effect of defect termination by H atoms during annealing.[16,19–21] For a $SiN_x$/P Cat-doped layer/c-Si structure, passivation quality relies not only on H defect termination but also on field-effect passivation, and increase in $T_{aB}$ might lead to increase in donor (activated P) concentration and resulting enhancement in field-effect passivation. Hayakawa *et al.* have reported that the most inactivated P atoms in a P Cat-doped layer exist in the forms of chemisorbed PH-, $PH_2$-, and $PH_3$ (coordinate bond)-type bonds with Si atoms, denoted as $PH_x$ (x = 1–3).[8] It has been reported that P and H atoms are major products, while PH- and $PH_2$- are minor products in the catalytic decomposition of $PH_3$.[22] We thus guess that the extraction of H atoms from $PH_3$ molecules by formation of $H_2$ molecules or the addition of H atoms to P atoms on a c-Si surface is possible mechanisms of $PH_x$ production.

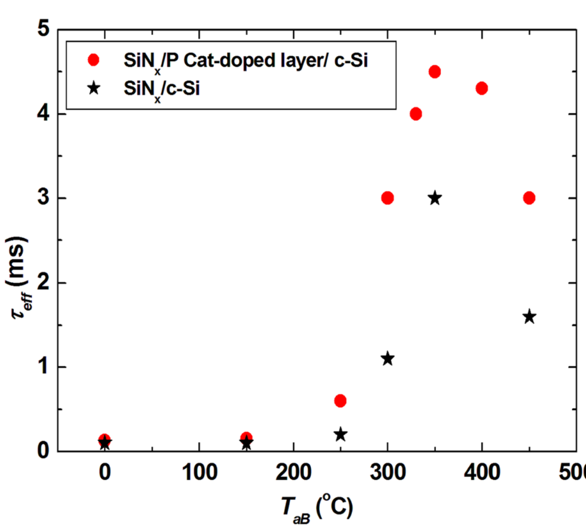


FIG. 3. The dependence of $SiN_x$/P Cat-doped layer/c-Si structures on $T_{aB}$ at an annealing time of 30 min. $\tau_{eff}$ of $SiN_x$/c-Si structures as a function of $T_{aB}$ is also shown for comparison.

$PH_x$ may decompose at high temperature, resulting in the release of P and H atoms. The released H atoms can diffuse to c-Si surface and terminate defects there, and the released P atoms act as donors and contribute to reinforcing field-effect passivation. There have been a number of literatures about the decomposition of P-H bonds using samples with $PH_3$ adsorbed on c-Si (100).[23–26] Yu *et al.* have reported that $PH_3$ molecules are partially dissociated at an annealing temperature of 275 °C for $PH_3$ adsorbed samples.[23] Tsai *et al.* have reported that $PH_3$ species are converted to $PH_2$ species in an adsorbed layer at annealing temperature >317 °C, and a P-H peak disappears when an annealing temperature exceeds 377 °C.[25] These facts indicate that $PH_2$ species are decomposed to P and H atoms at around 300 °C. We can guess that the released H atoms can make bonding with Si atoms and P atoms start to act as donors. In this study, as has been shown in Fig. 3, the $\tau_{eff}$ of a $SiN_x$/P Cat-doped layer/c-Si structure is much higher than that of $SiN_x$ c-Si structure when $T_{aB} \geq 250$ °C. This fact suggests that $PH_x$ starts to decompose efficiently at a $T_{aB}$ of 250 °C. This temperature is quantitatively consistent with the values of the literatures shown above. A $T_{aB}$ of 350 °C is sufficiently high for both $PH_x$ bond breaking in a P Cat-doped layer and defect termination by H in $SiN_x$ films, and higher $T_{aB}$ leads to the desorption of H atoms to atmosphere and resulting in the decrease of $\tau_{eff}$. The highest $\tau_{eff}$ can thus be obtained at a $T_{aB}$ of 350 °C for both structures.

On the other hand, contrary to our expectations, the results of the Hall effect measurement show that $N_D$ decreases by annealing. $N_D$ is $1.2 \times 10^{12}\,cm^{-2}$ before annealing, while it reduces to $0.9 \times 10^{12}\,cm^{-2}$ for samples with annealing at 350 °C for 30 min after depositing a-Si films, and to $0.7 \times 10^{12}\,cm^{-2}$ for samples with annealing at the same condition before depositing a-Si films. For the sample annealed after depositing an a-Si film, a possible reason for reduction in $N_D$ is the diffusion of H atoms from the a-Si film to the P Cat-doped layer, which can cause the formation of more $PH_x$ than $PH_x$ decomposition in a P Cat-doped layer and resulting reduction in $N_D$. Lower $N_D$ obtained in the sample annealed before depositing an a-Si film may be due to the oxidization of c-Si surface. In order to conduct annealing process, we have to take out the samples to atmosphere. Oxidation can inactivate P at surface c-Si and/or induce the formation of a thin Si oxide film containing P atoms on c-Si surface, which affect the results of the Hall effect measurement. In order to clarify this effect, the samples for the Hall effect measurement after P Cat-doping at 350 °C were put in air for 15 min before depositing a-Si films. By the additional air exposure, $N_D$ drops from $3 \times 10^{12}$ to $0.5 \times 10^{12}\,cm^{-2}$, which is a clear evidence of oxidation-induced reduction in $N_D$. We actually confirmed the formation of a $SiO_x$ film with a thickness of 1.1 nm and a refractive index of 1.5 at a wavelength of 630 nm on c-Si surface by using spectroscopic ellipsometry.

However, the oxidation of c-Si surface does not deteriorate the passivation quality of $SiN_x$/P Cat-doped layers on c-Si structure. The P Cat-doped layer/c-Si structures with or without annealing A (at 350 °C for 30 min) were put in air for one week. The sample was then passivated with a $SiN_x$ film, and annealed at 350 °C for 30 min (annealing B). For the sample without annealing A, $\tau_{eff}$ obtained of 4.4 ms does not differ from $\tau_{eff}$ of sample without air exposure. For the sample annealed with annealing B, $\tau_{eff}$ obtained is 6.4 ms. The addition of annealing A rather improves the passivation quality of a $SiN_x$/P Cat-doped layer structure by oxidation. We also investigated the effect of oxidation on $\tau_{eff}$ of $SiN_x$-passivated c-Si samples. Some c-Si wafers received annealing A at 350 °C for 30 min in $N_2$ atmosphere. The $\tau_{eff}$ of $SiN_x$/c-Si structures increases from 50 to 100 $\mu$s for samples without annealing B and from 3 to 3.5 ms for samples with annealing B. This indicates that the thermal oxidation of c-Si surface slightly improves the passivation quality of $SiN_x$ films on c-Si wafers. This improvement may be due to reduction in interface state by the formation of a $SiO_x$ film.[27–29] Furthermore, $\tau_{eff}$ of 250 $\mu$s is obtained for $SiN_x$/P Cat-doped layer/c-Si structure with only annealing A. This value is higher than that of a $SiN_x$/c-Si structure annealed with only annealing A. This result indicates that despite reduction in $N_D$ by oxidation, improvement in interface quality by oxidation and defect termination by H atoms released from $PH_x$ can contribute to increase in $\tau_{eff}$. After annealing B, besides the effect of defect termination by H atoms diffused from a $SiN_x$ layer, more $PH_x$ in a P Cat-doped layer can be decomposed, leading to higher donor concentration and more effective defect termination by H atoms, which results in higher $\tau_{eff}$.

On the other hand, as mentioned previously, $N_D$ obtained for an a-Si/P Cat-doped layer/c-Si structure is reduced by annealing at 350 °C for 30 min. Cat-CVD $SiN_x$ films also contain high amount of H atoms, which can diffuse from $SiN_x$ films to c-Si surface and terminate defects or recombine with P atoms to form more $PH_x$ during annealing B. Assuming that reduction in $N_D$ for the $SiN_x$/P Cat-doped layer/c-Si structures is the same as the case of a-Si/P Cat-doped layer/c-Si after annealing B, $N_D$ of a $SiN_x$/P Cat-doped layer/c-Si structure decreases by 25%. The sample undergoing both annealing A and B has $N_D$ of $\sim 5 \times 10^{11}\,cm^{-2}$, which is due to the effect of oxidation by annealing A and H diffusion during annealing B. This value of $N_D$ might be high enough for field-effect passivation. The fact that the $N_D$ of the sample receiving both annealing A and B is less than that with only annealing B indicates less effective field-effect passivation. However, the benefit of defect termination by H atoms might overcome the deterioration of field effect and lead to better $\tau_{eff}$ for the sample with both annealing A and B.

To understand the effect of annealing A on the passivation quality of $SiN_x$/P Cat-doped layers, c-Si samples Cat-doped at 80 °C for 1 min were annealed (annealing A) at various annealing temperatures ($T_{aA}$) for 30 min in the tubular furnace. Samples were then moved to the Cat-CVD system to deposit $SiN_x$ films. Finally, samples were annealed at 350 °C for 30 min (annealing B). Figure 4 shows the $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si structures after annealing A and B as functions of $T_{aA}$ and annealing time ($t_{aA}$) for annealing A. $N_D$ as a function of $T_{aA}$ is also shown. One can clearly see that $\tau_{eff}$ increases with $T_{aA}$ for samples both with and without process B. $\tau_{eff}$ increases when $T_{aA}$ increases and decreases for $T_{aA} \geq 400\,°C$. This is probably due to increase in $N_D$ at higher $T_{aA}$. The increase in $N_D$ is probably due to the decomposition of $PH_x$ at higher $T_{aA}$ and resulting activation of higher amount of P atoms. Additionally, the thermal oxidation of c-Si surface for the samples annealed at high temperature and defect termination by H atoms by annealing might contribute to the formation of a high-quality $SiN_x/SiO_x$/P Cat-layer and c-Si interface, resulting improvement in $\tau_{eff}$. Because the P Cat-doped layer is very shallow, too high $T_{aA}$ might lead to the desorption of H and P atoms to environment, which can result in decrease in $\tau_{eff}$ due to less effective defect termination and field-effect passivation. The complete

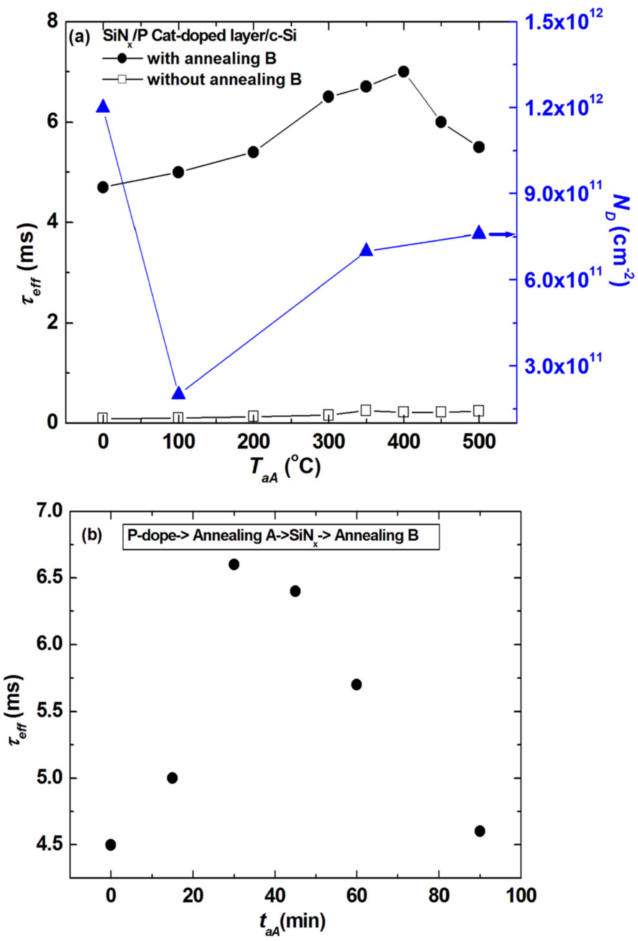


FIG. 4. $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si structures after annealing A at various $T_{aA}$ for 30 min and $t_{aA}$ at a $T_{aA}$ of 350 °C. Annealing B was conducted at 350 °C for 30 min.

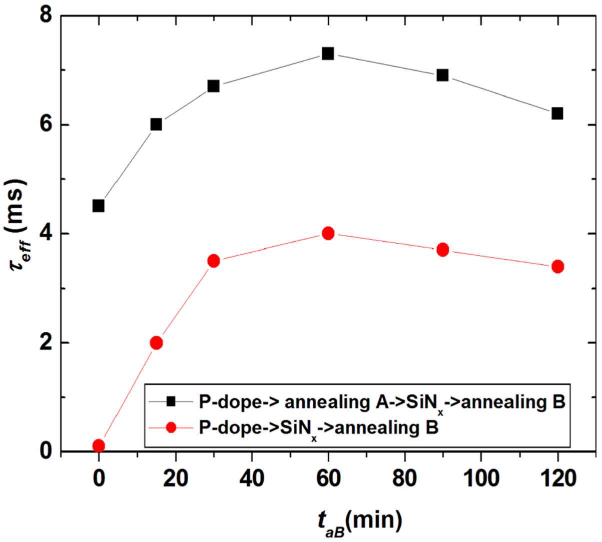


FIG. 5. $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si structures with and without annealing A as a functions of $t_{aB}$ at a $T_{aB}$ of 350 °C. Annealing A was conducted at 400 °C for 30 min.

thermal desorption of P atoms from $PH_3$ adsorbed c-Si surface at high temperature above 550 °C was also reported in Ref. 24, in which the desorption of H atoms at 400 °C has also been observed. The same tendency is seen in the annealing time dependence for annealing A, as shown in Fig. 4(b). $T_{aA}$ of 400 °C and $t_{aA}$ of 30 min are thus optimum conditions for annealing A needed to activate P in P Cat-doped layer without H and P desorption, and the highest $\tau_{eff}$ obtained for $SiN_x$/P Cat-doped layer/c-Si structures under the conditions. Figure 5 shows $\tau_{eff}$ as a function of the duration of annealing B ($t_{aB}$). We can see that $\tau_{eff}$ is still high for long $t_{aB}$. The tendencies of the variation of $\tau_{eff}$ for both samples are the same. Annealing for 30 min is enough to obtain high passivation quality for the samples. Further increase in $t_{aB}$ does not enhance more the activation of P atoms as well as defect termination. The instability of $\tau_{eff}$ due to increase in $T_{aB}$ and $t_{aB}$ may raise a doubt of reduction in $\tau_{eff}$ after long time exposure to air even at room temperature. We have confirmed that $\tau_{eff}$ of both $SiN_x$/c-Si and $SiN_x$/P Cat-doped layer/c-Si structures remain original values even after putting in air at room temperature for about 10 months.

In summary, a remarkably high $\tau_{eff}$ of ~7 ms, which corresponds to an SRV of ~2 cm/s, can be achieved for $SiN_x$/P Cat-doped layer/c-Si samples after annealing A and B. Compared with a $SiN_x$/c-Si structure, the insertion of P Cat-doped layer can reduce an SRV from 5 cm/s to 2 cm/s. The SRV of 4 cm/s has also been achieved when nearly stoichiometric $SiN_x$ films were deposited by plasma-enhanced CVD (PECVD) on 150–$\mu$m-thick 3–5 Ω cm n-type Czochralski (Cz) Si wafers after annealed in an industrial firing process.[30] An SRV of lower than 10 cm/s has been reported for 1.5 Ω cm p-type Si wafers passivated with stoichiometric $SiN_x$ films.[31] In these reports, they calculate SRV through $\tau_{eff}$ obtained by a contactless photoconductance tester allowing both transient PCD and QSSPC measurements at an $\Delta n$ of $1 \times 10^{15}$ cm$^{-3}$. Figure 6 shows $\tau_{eff}$ of a $SiN_x$/P Cat-doped layer/c-Si structure and a $SiN_x$/c-Si structure measured by QSSPC in transient mode. We observed $\tau_{eff}$ of ~7 ms for $SiN_x$/P Cat-doped layer/c-Si structure and ~3 ms for $SiN_x$/c-Si structure at a $\Delta n$ of $2.4 \times 10^{14}$ cm$^{-3}$. At a $\Delta n$ of $1 \times 10^{15}$ cm$^{-3}$, $\tau_{eff}$ is ~4 and 1.8 ms for $SiN_x$/P Cat-doped layer/c-Si and $SiN_x$/c-Si structures, corresponding to SRVs of 3.6 and 8 cm/s, respectively. Our SRV obtained in this study is the lowest level for n-type c-Si passivated with $SiN_x$ films without firing process or with only low temperature process, which is acceptable for fabrication of a-Si/c-Si hetero-junction solar cells. The remarkable value of our SRV obtained for $SiN_x$/P Cat-doped layer/c-Si structure highlights the promising application of Cat-CVD technique in high-efficiency n-type c-Si based solar cell fabrication.

### B. Effect of $T_{s\text{-}dope}$ and doping duration on the passivation characteristic of $SiN_x$/P Cat-doped layer/c-Si structure

High $T_{s\text{-}dope}$ can activate P atoms as donors in a P Cat-doped layer.[8,9] This can contribute to improvement in field-

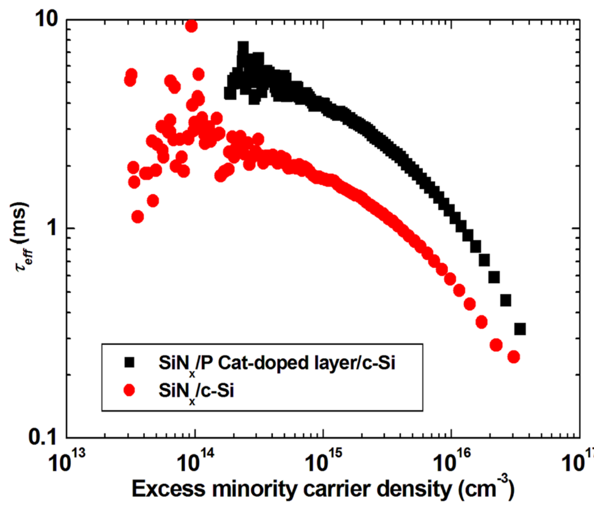


FIG. 6. $\tau_{eff}$ as a function of excess carrier density in a $SiN_x$/P Cat-doped layer/c-Si structure and a $SiN_x$/c-Si structure.

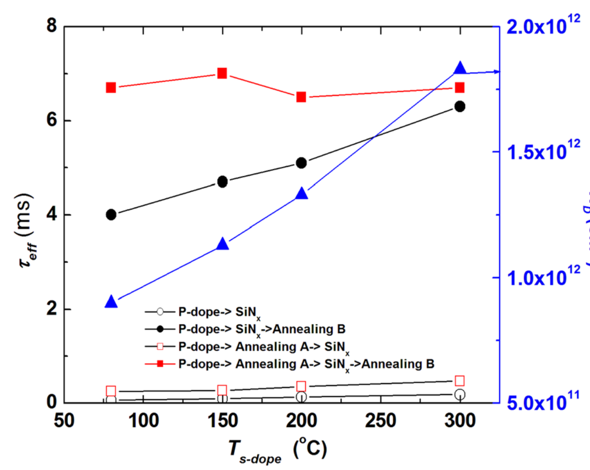


FIG. 7. $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si samples as a function of $T_{s\text{-}dope}$. $N_D$ as a function of $T_{s\text{-}dope}$ before annealing A is also shown. Annealing A was conducted at 400 °C for 30 min and annealing B was conducted at 400 °C for 30 min.

effect passivation. In this investigation, we prepared P Cat-doped samples at various $T_{s\text{-}dope}$ for 1 min. Figure 7 shows $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si samples as a function of $T_{s\text{-}dope}$ with and without annealing A. $N_D$ as a function of $T_{s\text{-}dope}$ before annealing is also shown. $N_D$ increases with increase in $T_{s\text{-}dope}$. This may suggest that H atoms desorb from c-Si surface during P Cat-doping at high $T_{s\text{-}dope}$ due to the extraction of adsorbed H atoms on c-Si surface by atomic H and/or $PH_3$.[8,32,33] As we mentioned above, Umemoto *et al.* have reported that major products in the catalytic decomposition of $PH_3$ molecules on a heated tungsten catalyzer are P and H atoms.[22] Here, we suppose that the reaction of atomic H with adsorbed H and/or $PH_x$ on a c-Si surface and/or $PH_x$ bond breaking are possible mechanisms for H release at high $T_{s\text{-}dope}$. This process might assist P activation. We can see lower H concentration in a sample doped at a $T_{s\text{-}dope}$ of 300 °C in a SIMS profile, as shown in Fig. 8 later. The increase in $N_D$ makes small increase in $\tau_{eff}$ before annealing. It contributes significantly to improvement in $\tau_{eff}$ for the sample doped at high $T_{s\text{-}dope}$ when the samples were annealed with annealing B. The samples doped at a $T_{s\text{-}dope}$ of 300 °C, which shows $N_D$ of $\sim 2\times10^{12}\,cm^{-2}$, can reach the highest $\tau_{eff}$ of ~6 ms.

Figure 7 also shows $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si samples with annealing A and B as a function of $T_{s\text{-}dope}$. One can see that $\tau_{eff}$ does not depend on $T_{s\text{-}dope}$, and all the

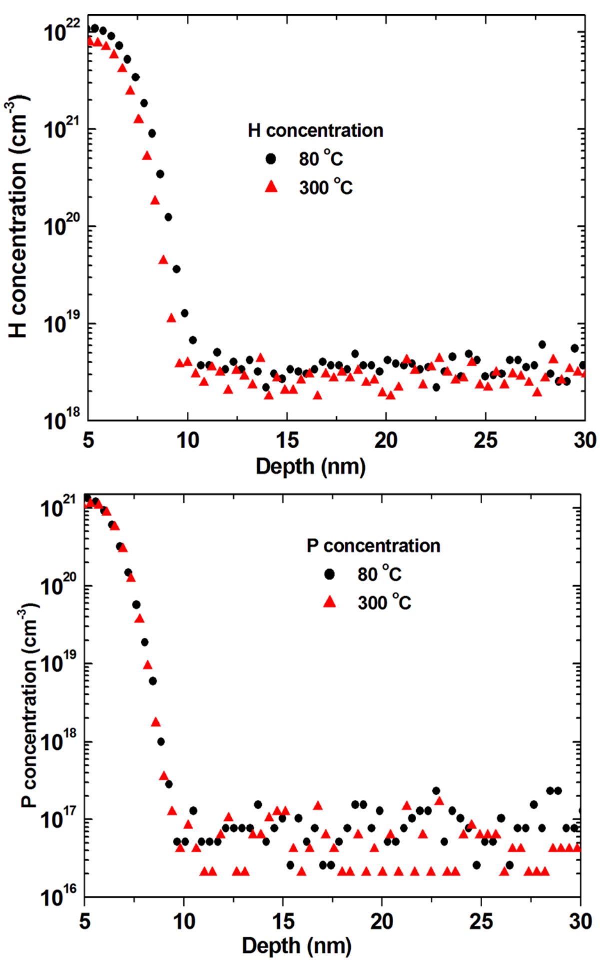


FIG. 8. SIMS profiles of P and H atoms in the samples doped at 80 °C and 300 °C without annealing.

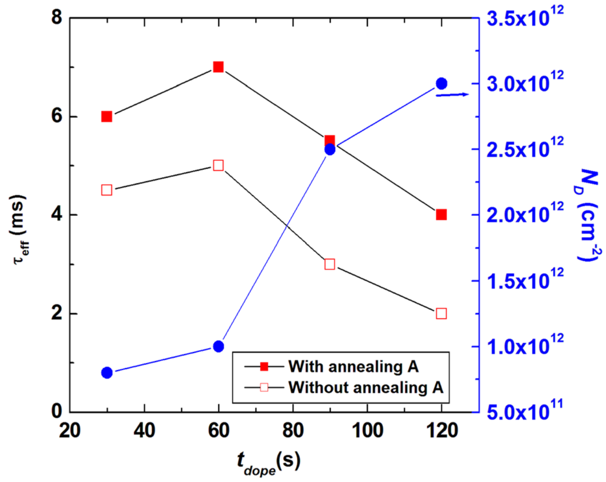


FIG. 9. $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si samples as a function of $t_{dope}$ with and without annealing A. $N_D$ before annealing is also shown. Annealing A was conducted at 400 °C for 30 min and annealing B was conducted at 400 °C for 30 min.

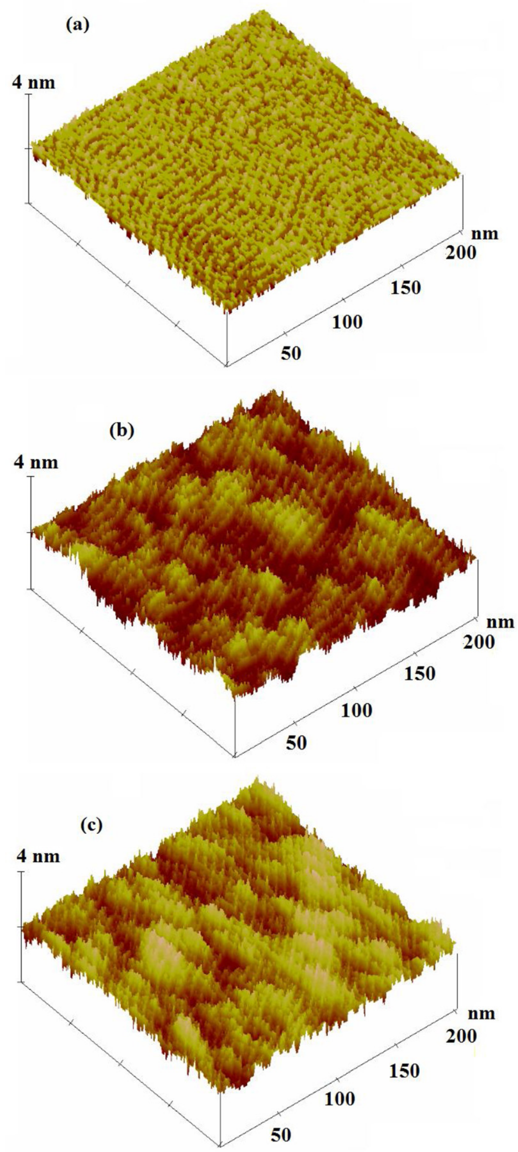


FIG. 10. Surface AFM images of (a) bare c-Si and c-Si Cat-doped for (b) 60 s and (c) 90 s.

samples have constant and high $\tau_{eff}$ of 7 ms. This result suggests that P donor concentration is constant in all the samples with annealing before and after $SiN_x$ deposition. Figure 8 shows the SIMS profiles of samples with P Cat-doping at $T_{s\text{-}dope}$ of 80 and 300 °C before annealing. We can see no significant difference in the two profiles, suggesting that the activation ratio of P atoms in the two samples is similar.

$N_D$ of a P Cat-doped layer also increases with $t_{dope}$.[9] We should therefore concern the effect of doping time on $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si samples. The samples were doped at 80 °C for 30, 60, 90, and 120 s. The effect of annealing before depositing $SiN_x$ films was also investigated for these samples. Figure 9 shows the $\tau_{eff}$ of $SiN_x$/P Cat-doped layer/c-Si samples as a function of $t_{dope}$ with and without annealing A. $N_D$ without annealing is also shown. Although $N_D$ increases with increase in $t_{dope}$, $\tau_{eff}$ decreases when $t_{dope} \geq 60$ s. For the sample doped for 30 s, $\tau_{eff}$ is low due to low $N_D$. A possible reason for the low $\tau_{eff}$ observed in the samples with $t_{dope} \geq 60$ s is the effect of surface etching by radical species during Cat-doping process. Figure 10 shows the surface AFM images of bare c-Si and c-Si doped for 60 s and 90 s. The surface of bare c-Si has a root-mean-square roughness ($R_{rms}$) of ~0.09 nm with the average height of 0.3 nm. As shown in Figs. 10(b) and 10(c), the two P Cat-doped samples have more roughened surfaces, and the surface receiving longer Cat-doping is more seriously etched. The sample with a $t_{dope}$ of 90 s has a $R_{rms}$ of 0.24 nm and average height is 0.9 nm, while they are 0.21 nm and 0.7 nm, respectively, for the sample doped at 60 s. Excess $t_{dope}$ thus rather deteriorates the interface quality, and an optimum $t_{dope}$ exists to obtain high $\tau_{eff}$ for $SiN_x$/P Cat-doped layer/c-Si structure.

## IV. CONCLUSION

In conclusion, an extremely low SRV of 2 cm/s can be obtained for the $SiN_x$/P Cat-doped layer/n-c-Si structure. Annealing plays important roles for improving the passivation quality of $SiN_x$ films and enhancing field-effect passivation. Additional annealing, before depositing $SiN_x$ films (annealing A), enhances the activation of P dopants in a P Cat-doped layer and improves $\tau_{eff}$. Increase in $T_{s\text{-}dope}$ increases sheet carrier density, resulting in the improvement of $\tau_{eff}$. $\tau_{eff}$ of $SiN_x$/P Cat-doped/c-Si sample decreases with excessive $t_{dope}$ due to etching effect by radical species during P Cat-doping. An SRV of 2 cm/s is obtained under optimum Cat-doping and annealing conditions for $SiN_x$ films on n-type c-Si wafers, indicating the potential application of Cat-CVD in producing high-efficiency c-Si solar cells. We emphasize that the use of a high transparent $SiN_x$ passivation layer with a P Cat-doped layer can enhance the performance of n-type c-Si solar cells, particularly of back-contact solar cells.

## ACKNOWLEDGMENTS

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